"The Specific Resistance and other Properties of Sulphur." By JAMES MONCKMAN, D.Sc. Communicated by Professor J. J. THOMSON, F.R.S. Received November 10,—Read December 6, 1888.

Resistance.

It is well known that sulphur in a solid state insulates electricity of very high potential, and conducts heat badly; also that it undergoes a curious series of changes when heated—melting at about 120° C., becoming thicker at 200° to 250°, more liquid at 250° to 300°, and boiling under atmospheric pressure at 440°. During the past three terms I have been engaged in the Cavendish Laboratory in trying to determine whether these changes are accompanied by corresponding ones in the electrical resistance and other properties of the element.

I expected that the changes would be within the limits of an insulating body, hence my first experiment was designed to test the insulating power for frictional electricity.

Two platinum wires were placed in a beaker of melted sulphur at a distance of about 1 cm. apart, one being connected to an electroscope, the other going to earth. When the sulphur became solid the leaves of the electroscope remained open on charging for a considerable time, but fell at once if any portion of the sulphur between the wires was liquid. To avoid all discharging by the flame used in melting the sulphur, the platinum wires were fixed to an ebonite rod at the proper distance apart. After melting the sulphur the flame was removed to a distance and the wires placed in the liquid. The discharge was complete and, apparently, as sudden as when contact was made with a wire.

The same experiment was tried with paraffin, and the discharge found to be very slow.

Seeing then that the resistance was removed by melting the sulphur into the region of conductors, it became necessary to find some method that could be used for conductors of very high resistance.

At Mr. Glazebrook's suggestion I tried placing the wires in melted sulphur in circuit with a high resistance reflecting galvanometer and a set of accumulators giving a total electromotive force of 60 volts. With platinum wires in the sulphur no reliable results could be obtained as the current quickly fell away.

While thus engaged my attention was directed to a paper by M. Duter ('Comptes Rendus,' vol. 106, 1888, p. 836), in which he describes some experiments on boiling sulphur. Platinum he found to be attacked by the sulphur, but gold gave good results; no measurements were, however, given. Following Duter's plan I used

gold electrodes, but failed to get a steady current to pass; neither did ordinary carbon plates answer any better.

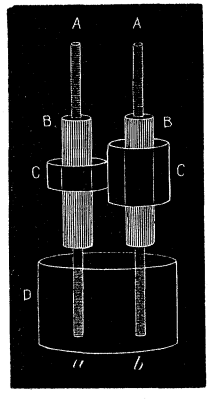
Having some graphite rods which had been procured from Hogarth and Hayes, Keswick, for some experiments on carbon, I tried two of them, and obtained a perfectly constant flow of electricity even at the boiling point. The change in the resistance between melting point and boiling point was so great that it was difficult to arrange a method that would give reliable readings. In the Cavendish Laboratory, where this work was done, we have a set of 26 accumulator cells which when charged give a potential of about 60 volts. This is conducted to all the rooms, and is so arranged that we can use any number of cells, so that we can vary the potential from 60 volts to about $2\frac{1}{3}$ volts.

When the sulphur was melted (125° C.) 60 volts gave a deflection with a reflecting galvanometer of 11,770 ohms resistance of only half a millimetre on the scale, while at 440° C. one cell gave a deflection of 60 mm.

By changing the number of cells, and measuring the potential by a Thomson's graded voltmeter at each change, the results given in the following tables were obtained.

The graphite rods were carefully insulated from each other by hard glass tubes, over which shorter pieces of tube of unequal length were placed, and fixed with plaster of Paris, the object being to give as much insulating surface as possible. A cell of mica was placed around the projecting part of the graphite rods to render the path of the current fairly parallel; the ends were left open to allow free access of sulphur and to prevent vapour taking the place of the liquid when ebullition commenced.

The form of the mica cell was preserved by an outer cell of thin glass.



In the figure, A, A are the graphite rods, B, B glass tubes, C, C

larger ones, D mica. The exposed ends were filed flat, and fit loosely into the tube D. The dimensions are: length, 30 mm.; width, $3\frac{2}{3}$ mm.; distance, 7 mm. between the free ends, *a*, *b*.

The change of resistance was so great and fell so quickly at the higher temperatures that it gave rise to a suspicion that the increase of conductivity might arise from particles of the rods being torn off and mixed with the sulphur. To test this, the rods were placed in a second tube of boiling sulphur, so that when placed in the tube of pure sulphur they might not reduce the temperature of the liquid. After removing and allowing the adhering liquid to flow back, they were placed in the other vessel, and the current passed at once. The deflection was the same as before, and steady, neither did the rods appear to be acted upon in any way.

Hence we concluded that the change was in the sulphur itself.

Resistance.—Ordinary roll brimstone :—

Temperature.	Potential.	Deflection.	Reduced to one standard by multiplying by 60/*v*.
440°	$2\frac{1}{3}$	60	1560
300	,,	12·5	325
270	,,	2	52
250	,,	1	26
250	55	10	24
223	..	3	7
195	60	6	6
150	,,	5	5
140	,,	2	2
125	,,	0·5	0·5

Another specimen gave slightly different numbers, but of the same order.

With precipitated sulphur the resistance was considerably higher.

440°	4·1	35	512
350	,,	5	73
335	..	3	44
335	8·2	7	51
290	54	5	5·5
280	,,	2·5	2·8
260	,,	0·5	0·55
125	..	could get up a swing only.	..

The specific resistance may be calculated from these tables, using the quantities previously given, namely, l. 30 mm., w. $3\frac{2}{3}$, d. 7; and

the value of each scale division is 0·03$\dot{3}$ milliampère of current passing per second. Hence since E/R = c we get—

$$\frac{4{\cdot}1}{R} = 0{\cdot}00000116\dot{6} \text{ ampère}$$

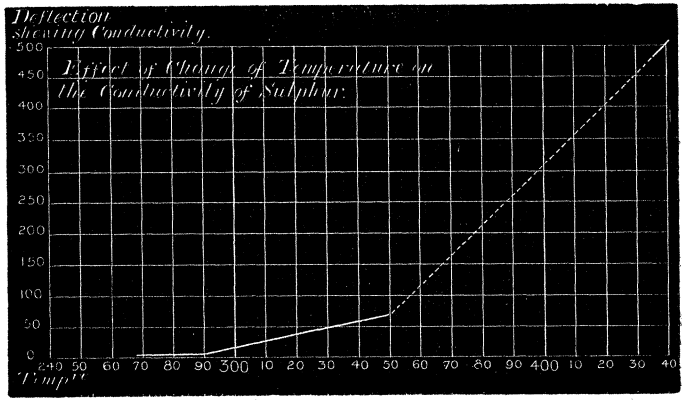
$$R = 3{,}553{,}448 \text{ ohms.}$$

$$\text{Specific resistance} = R \times \frac{30 \times 0{\cdot}36\dot{6}}{0{\cdot}7} = 1{\cdot}57 \times R = 5{,}600{,}000$$

nearly, or 5×10^5 ohms at 440°; at 260° it is nearly 1000 times that number, or 5×10^8.

Roll sulphur gives the same resistance at 125°, that is, 5×10^8; while at 440° it is one-third precipitated sulphur, or $1{\cdot}6\dot{6} \times 10^5$.

The accompanying curve shows the conductivity of precipitated sulphur. At 290° C. there appears a sharp bend in the line. Up to that point the conductivity rises to 5·5, becoming 51 in the next 45°, after which it rises rapidly. This bend coincides fairly with the second fluid state, and probably indicates some molecular change which appears to produce similar irregularities in its other properties.

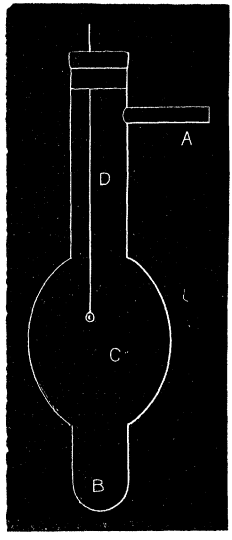


Boiling Point.

The first of these tested was the effect of pressure upon the boiling point.

The apparatus used is given in the next diagram, the sulphur being placed in the space B, whilst the larger spaces, C and also D, were surrounded with sheet asbestos to prevent rapid radiation. The tube A was connected with an air-pump and mercury gauge.

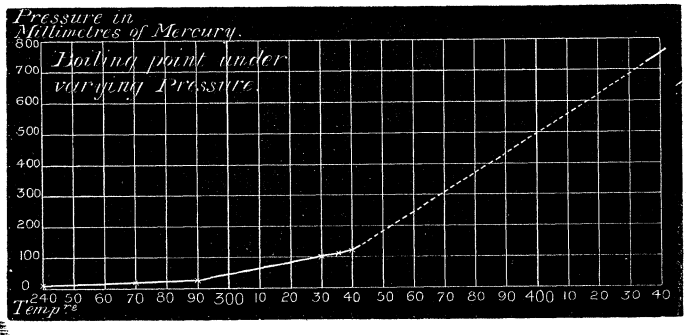
When the sulphur in B was heated, on exhausting the air the first time there was a violent temporary evolution of gas at 240° C. if the pressure was 23 cm.; but if the air was withdrawn until the gauge registered 1 mm., this ebullition took place at 150° C. This escape of



gas took place even after the sulphur had been boiled at the ordinary pressure of the atmosphere, and also after a considerable evolution at 150° when, apparently, all gas was driven away, a second one occurred on raising the temperature.

One or two precautions are necessary in order to get good results. The sulphur is a bad conductor of heat, and therefore one part of it near the flame may be many degrees above another in the interior. The vapour from the hotter bursts through the cooler liquid and rising into the space C causes a higher temperature to be registered than the true one. By reducing the flame, and by surrounding the portion B with a conductor such as mercury for temperatures below 350°, the heat can be regulated and spread until this is avoided.

The curve is drawn from data furnished by experiments at various temperatures up to 340° only, one temperature being taken above that,



namely, 440°. There appears the same change at 290° as in the previous curve which it closely resembles.

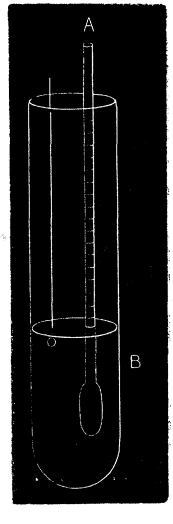
At one time I thought that sulphur might be added to the list of bodies given by Ramsay and Young in their paper on "Evaporation and Dissociation" ('Phil. Trans.,' 1884, p. 461) as a means of obtaining a range of temperature above 350° up to 440°. The chief difficulty arises from the overheating, before mentioned, and the danger of breaking a vessel of solid sulphur on reheating. The first can be avoided by carefully heating, and the second is very much reduced when the sulphur is allowed to solidify under much diminished pressure.

The two curves given above are so nearly identical that one naturally suspects that the former is produced by the increased mobility indicated by the latter, and that if the measurements for resistance were taken at each temperature when the liquid was under pressure so diminished that ebullition took place, the mechanical agitation of the particles would produce a decrease of the resistance in addition to that due to the temperature alone, and carry off the charge somewhat after the manner of air and a pointed conductor in electricity of high potential.

That this was not so was proved by placing the graphite rods in the vessel used for the last experiments. After heating and exhausting to expel the gas measurements were taken at various temperatures; in one set the sulphur boiled under diminished pressure, and in the other set the air was admitted. No difference could be detected.

Expansion.

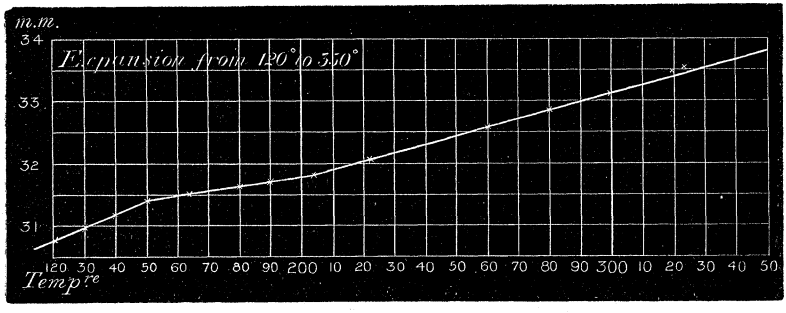
Having failed to obtain measurements with the specific gravity



bottle from the difficulty of preserving the bottle on remelting the sulphur, a tube was used shown in the figure at A. The capacity of the bulb was 13·6 cm. The second vessel contained sufficient mercury to cover the bulb of A, and the stem to the point to which the sulphur rose on heating.

The bulb was filled with sulphur, and the whole of it kept beneath the surface of the mercury except when a reading was taken.

From several series of experiments the curve was prepared.



Chemical Affinity.

If the changes previously noticed are produced by some change in the molecules of the element, it will probably show itself in the action of sulphur when strips of metal are exposed to its attack. We know that some metals are acted upon at ordinary temperatures in a slight degree, and with increased energy as the temperature rises. Others do not appear to be changed until a high point. It therefore appeared probable that by carefully watching strips of different metals exposed to sulphur at various temperatures, it might be discovered whether there was any point of sudden increase, and if so what relation it bore to the curves already obtained.

A test tube was used for the sulphur, and a strip or piece of the metal having been placed in it, the tube was immersed in heated mercury.

Temperature.	
120° C....	After expelling all the air by a stream of coal-gas, sodium was dropped in. Took fire.
180°.....	Heated four hours with occasional shaking. Hg, Cu, and Pb slowly attacked. Mg, Zn, and Sn not.
245 to 270°	Hg formed a dark malleable mass, filled with globules of the metal. Cu more readily acted on.

Temperature.	
290 to 310°	Cu almost eaten away.
	Pb as before.
	Mg, Zn, and Sn not attacked.

Again pieces of copper, of equal sizes and weights, were cut from the same sheet. After having been carefully cleaned and weighed they were exposed to sulphur at different temperatures for 15 minutes, after which they were carefully cleaned and re-weighed.

Weight of copper used.	Temperature.	Loss of weight.	Rise of temperature.
(1) 11·34 grams..	240°	0·89	12°
(2) „ ..	280	0·92	11
(3) „ ..	300	1·62	30

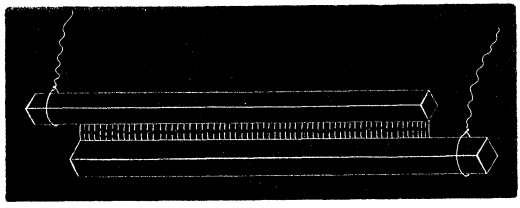
The last column gives the increase of temperature due to the union of the copper and the sulphur. It occurred two minutes after the cold copper was introduced. At first there was a fall of 4° in the two first experiments, and 5° in the last; this was followed by a rise. The lamp was withdrawn when the temperature rose to that at which the experiment commenced. At the end of two minutes the rise given in the fourth line was observed.

It appears, therefore, that there is a gradually increasing action up to 290°, or about that temperature, and above that a considerable increase. The point of change in resistance, 290°, appears to be one of considerable importance, carrying also the fluidity, boiling point, and chemical affinity, &c.

Action of Light on Sulphur.

That the metals of the same group in the arrangement according to the Periodic Law have properties in common is well known. Thus chlorine, bromine, and iodine belong to the same group, and are in many respects very similar bodies. Sulphur belongs not only to the same group as selenium, but is the next element in front of it. Naturally, therefore, we expect that they will have properties in common, and possibly the action of light in the case of selenium may be shared in an inferior degree by sulphur. This appears more probable from the well-known fact that a saturated solution of sulphur in bisulphide of carbon is rendered turbid by direct sunlight, part of the sulphur being changed and becoming insoluble in that liquid. A portion of the sulphur undergoes the same change when exposed to a high temperature. In order that the sulphur used in the experiment might be as sensitive as possible to light, it appeared desirable

that only pure soluble sulphur should be used, and that great care should be taken not to raise the temperature in melting it so high as to produce any of the insoluble modification.



Two rectangular graphite rods were placed parallel to each other, the one projecting about an inch at one end, the other at the other end.

The edges were turned towards each other, as shown in the figure, leaving a space of one millimetre, which was filled with melted sulphur. This was levelled off with a hot iron to make the portion between the corners as thin as possible.

When one of the projecting ends was placed in contact with a charged electroscope, the other being to earth, the charge fell more quickly when illuminated, on the average as 5 is to 4.

As little reliance can be placed on these experiments, a quadrant electrometer was charged, and the graphite rods, separated by sulphur, inserted between the binding screws, so that the negative quadrant was connected with the positive one through the sulphur (1·5 cm. long, 1 mm. thick, and 1 mm. broad).

The electrometer was charged to the same potential in each experiment in a series and allowed to run down for a certain time. Sunlight was allowed to fall on the sulphur, but shaded from the rest of the apparatus; when not required the ordinary window blind was drawn down.

Of course the electrometer and sulphur were protected from induction by surrounding bodies by wire screens.

The following three series of readings were taken on different days, and in one or two cases clouds interfered with the experiment, especially in No. 8, when the light was considerably shaded by cloud.

	Scale deflection at the beginning.	Time.	Fall in scale divisions.	State.
		minutes.		
1st series (1) .	180	30	20	Dark.
(2) .	,,	15	20	Light.
(3) .	,,	35	18	Dark.
2nd series (4).	300	15	25	Light.
(5).	,,	17	25	,,
(6).	,,	15	20	Dark.
(7).	,,	15	19	,,
(8).	,,	15	20	Light.
3rd series (9).	200	15	14	Light.
(10)	,,	15	17	,,
(11)	,,	16·5	16	,,
(12)	,,	15	10	Dark.
(13)	,,	15	10	,,

The first and second series were alternated dark and light in the same set of experiments to see that no permanent change was produced and mistaken for the effect sought. In the first the time varied and the deflections were allowed to fall the same distance; in all the others the time was the same and the fall varied.

The method of performing the experiments made it possible that the effect might be produced by the heat of the sun and not by the light. The variation in temperature observed on a delicate thermometer was about 1° C. To eliminate the effect of heat, a long series of observations was made in the dark, whilst the temperature was raised slightly by placing a Bunsen flame 4 or 5 inches away from the screen protecting the sulphur, and the heat radiated by placing an iron spiral in it, then one of copper, and lastly a fine clay tile.

The range of temperature was 15·2° C. to 17·1° C. in the first ten experiments, in which the heated ones fell rather more slowly than those at a lower temperature. In the next seven observations the range was 14·8° C. to 18° C., the fall being exactly the same in each.

There yet remained the possibility that the light falling on the wires which held the rods caused the charge to escape more quickly into the air. When, however, the sulphur was removed, the effect produced by the light on the portions of wire exposed to its influence was too small to produce any change in the rate of fall.

Hence it appears that although selenium is the body most sensitive to the action of light, it shares its property with its neighbours, and the three elements (constituting the same group), sulphur, selenium, and tellurium, are all similarly acted upon, furnishing another example

of the importance and beauty of the law which classified them together.

During the course of this work I have often consulted Professor J. J. Thomson, F.R.S., and received many valuable suggestions and some corrections, for which I desire to acknowledge my obligation.

Addendum. May 22, 1889.

It having been suggested that the passage of the current at high temperatures through roll and precipitated sulphur was caused by the presence of impurities, and not by any change in the properties of the sulphur itself, that some of the impurities distil over with the element, especially sulphuric acid, compounds of mercury and selenium, whose presence would be quite sufficient to account for the effects given by the specimens used in the previous experiments, it was necessary to btain the purest possible specimens of sulphur, and with this object no pains have been spared.

As there also arose the question whether a liquid, being neither a metal nor an electrolyte, could conduct an electric current, it appeared to be preferable to try various methods of purification, and to compare the results obtained.

To make this comparison more valuable, the methods should not be simply variations of the one system, but proceed upon distinct lines, so that any impurities, left after all possible care had been used, should be different in the different specimens, and in the measurements there would appear the effects due to distinct bodies, and if so, give some indication of the presence, in one or other of the portions used, of some foreign body changing the electric properties of the melted sulphur differently from the cases in which that particular body could not possibly occur. Three methods of purification were employed:—1st, solution, crystallisation, and distillation; 2nd, distillation, without solution, in an atmosphere intended to remove hydrogen compounds; 3rd (pure soluble bodies only were used, easily tested chemically), precipitation, washing with water, and distillation.

In numbers 1 and 2, foreign bodies acting upon sulphur were added and afterwards removed; they were different bodies, and if not perfectly removed might be expected to change the conductivity according to their own individual properties. In number 3 no such body was introduced. Consequently, if 1, 2, and 3 were alike in their resistances at various temperatures, it must arise from changes in the one body common to all three, namely, sulphur.

Before giving further particulars of these three methods, I wish to describe experiments undertaken to prevent the electrodes and the containing vessels from spoiling the liquid after it had been purified.

In the course of the work it was found that the vessels in which sulphur was boiled for any length of time were attacked. Ordinary test-tubes invariably gave way, becoming coated internally with a thin black film, which remained fixed to the glass.

Ordinary tubes and glazed porcelain under the same circumstances showed a number of dark spots, which proved to be sulphide of iron; even combustion-tubing did the same thing.

All these experiments had been made with the flame of a bunsen lamp acting directly upon the vessel containing the sulphur, and it appears that no material will resist the attack of that body under such conditions. It seems to be caused by over-heating a portion of the vessel from which the liquid has been separated by the vapour, when bubbles are formed. When the liquid falls back upon this over-heated surface, chemical action commences.

Further experiment, however, showed that when combustion-tubing, or retorts of Bohemian glass, are protected from the direct action of the flame, sulphur may be boiled or distilled in them without any action whatever taking place.

Investigations were also made on the nature of the electrodes, by means of which a current could be made to pass through sulphur, and upon the best form to be used to avoid chemical action. In the previous work I used ordinary thin platinum wire, and failed to get a current to pass.

In repeating this experiment I used a wire of one millimetre diameter, which had been exposed to great heat for a considerable length of time, and found that the current passed readily.

The same thing took place when some thin, very hard, carbon rods were substituted for the platinum. The liquid was, however, dirtied by particles of carbon torn away from the rods, and consequently I have not considered the numbers obtained worthy of being recorded, but simply the fact that with hard carbon rods for electrodes, sulphur will conduct; probably electric lamp filaments may prove good enough to resist disintegration, if not too thin for the purpose.

To test the effect of sulphur upon the electrodes, the containing vessel was placed in a second one, half filled with mercury, which was kept boiling several hours; this produced a steady temperature of 350°. The platinum electrodes were immersed in the liquid, and after allowing them to remain undisturbed until the whole mass had assumed the proper temperature, measurements were taken at stated intervals. The method was to use a steady electromotive force, with the sulphur in circuit, and a high resistance galvanometer. The numbers given below show a conductivity increasing with the time of contact between the electrodes and the hot sulphur. After the experiment I found that the platinum was considerably discoloured.

Table showing the action of Heated Sulphur upon Platinum Electrodes.

After an exposure of—		Deflection produced by a constant electromotive force.
60 minutes	.....	22 scale divisions.
90 ,,	.....	29 ,,
120 ,,	.....	32 ,,
140 ,,	.....	33 ,,
200 ,,	.....	40 ,,
260 ,,	.....	43 ,,
275 ,,	.....	44 ,,

Lastly, the same graphite rods were used as in the previous experiments. These electrodes had been repeatedly exposed to high temperatures, and also boiled many times in sulphur. After being kept at temperatures varying probably not more than from 400° C. to 440° C. during five hours, the conducting power of the liquid was practically the same as at first.

Thus, at 12.50 P.M. (boiling) the deflection was 290 scale divisions. The flame was then slightly reduced, and at—

1.20 P.M.....	260 scale divisions.
3.30 P.M.....	150 ,,

The flame was then raised again, and at—

4.30 P.M.....	220 scale divisions.
5.30 P.M. (boiling)	280 ,,
5.50 P.M. ,,	280 ,,

New graphite electrodes were next tried, and found to discolour the sulphur considerably; but the resistance was increased. In all cases the current passed. The objection to using the same electrodes, even after using great care in cleaning them in the different liquids, and in that way contaminating them, and the impossibility of getting new ones that would do without previous boiling in sulphur, caused me to abandon their use altogether, and to depend upon a short exposure of platinum instead. The conclusion, determined by the work described, was that using combustion-tubing for boiling and well-cooked graphite electrodes, the change produced by chemical action is practically nothing, even after boiling several hours, if the containing vessel be protected from the direct flame, and that in the case of platinum electrodes, if the observations are taken immediately they are inserted into the liquid, the action is slow enough to allow measurements to be taken without fear of error.

Purification of the Sulphur.

In the first method, for which I am indebted to Dr. Ruhemann, of the Chemical Laboratory, Cambridge, bisulphide of carbon was purified by being shaken with a little mercury and allowed to stand. It was afterwards distilled over dry calcium chloride. These operations were repeated until the liquid was separated from other sulphides and from water. It was then saturated with sulphur and half of the liquid distilled off. On cooling, crystals of sulphur formed. These were removed and washed with fresh bisulphide to remove any impurities that might have been left on their surfaces by the evaporation of the adhering mother-liquid. They were then carefully broken up and placed in a vacuum to remove as much of the bisulphide as possible before distilling. After remaining so for several days, they were distilled *in vacuo* several times, the first portion coming over, and that portion remaining behind being rejected in each case.

The substance thus produced was of a beautiful light yellow colour, and melted into a perfectly clear, transparent liquid, about the colour of olive oil; at higher temperatures it assumed the tint of port wine. No traces of sulphuric acid, nor of chlorides, could be found, and the absence of selenium was proved in the original substance.

The only objection to this method of working is the presence of a body whose solvent power for sulphur is so great, and the possibility that the last traces are not removed even by repeated distillations *in vacuo*.

The second method consisted in distilling precipitated sulphur in an atmosphere of chloride of sulphur, which removes hydrogen compounds. After repeating this several times, it was distilled *in vacuo*. As before, the middle portion only was retained. This method has been found to give good results in the hands of some experimenters, but I found very great difficulty in removing the chloride, being obliged to reduce the body to a fine powder, and wash with water, and finding this insufficient, finally distilled over a few small pieces of pure zinc *in vacuo*, after which it was redistilled.

This specimen was distilled altogether eleven times.

The third method is the one used by Professor Threlfall, who takes hyposulphite of soda, free from selenium, and dissolves it in distilled water, then precipitates the sulphur by means of pure hydrochloric acid.

The reaction is shown by the well-known equation—

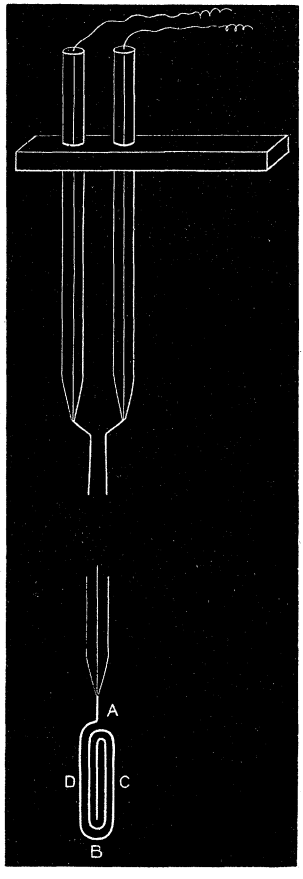
$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + H_2O + S.$$

All the substances produced, being either soluble in water, or gas evolved during the reaction, except the sulphur itself, can be washed out with pure water.

To avoid the addition of any objectionable body, no attempt was made to precipitate the sulphur from the sulphur dioxide, hence half the sulphur present was lost.

Thus it will be seen at once that a considerable quantity of the salt was required to produce a very small quantity of pure sulphur. 14 lbs. of the hyposulphite were dissolved, filtered, and decomposed by acid, then washed until free from salts and acids, dried, and distilled several times. When the residue appeared to be perfectly free from foreign matter it was repeatedly distilled *in vacuo*, the middle portion being removed.

In this method the only solvent was water, and the other bodies produced could be tested for by delicate chemical reactions. I believe that the three methods described fulfil the requirements mentioned in an earlier portion of this paper, giving as pure sulphur as can be prepared, but at the same time, the bodies that may have escaped removal will differ in each specimen.



An improvement was introduced into the insulation of the electrodes. The platinum wires were fused into glass tubes from 12 to 14 inches in length. These were fixed into hard dry wood at a distance of several inches from their ends. In this way the only part that can possibly conduct is removed further from the source of heat.

The ends of the electrodes were flat plates, formed by bending the platinum wire upon itself three or four times, and then welding it together, also for greater security a strip of platinum-foil was welded to the back of each.

The length of AB was 3·35 cm., the width 0·45 cm., and the distance apart 0·2 cm.

The tube in which the sulphur was boiled was formed by fusing up the end of a piece of combustion-tubing about 9 inches long, and wide enough to allow the glass tubes to be inserted in the sulphur without danger of touching the sides, and thus forming a circuit through hot glass.

It was surrounded to the height of 3 inches by a copper tube, closed at the bottom, the intervening space being filled with sand.

To avoid the chemical action which has been shown to take place when platinum is exposed for any length of time to sulphur at a high temperature, the electrodes were kept out of the liquid until everything was ready for taking a reading; they were then inserted, and the readings having been taken as quickly as possible, they were removed.

At the end of each set of experiments the wires were examined and found in every case to be free from any appearance of the dark film observed in the preliminary work.

Before introducing them into the next specimen of sulphur they were ignited in the blowpipe-flame until perfectly clean.

The method used was to place the sulphur in circuit with a battery and a high resistance galvanometer (R 11,700 ohms). In order to avoid chemical action it was considered better to reduce the number of observations and to commence with the boiling point.

At 440° C.	pure sulphur	gave a	deflection	of	545 to 570 divisions.
350° C.	,,	,,	,,		75 ,,
300° C.	,,	,,	,,		15 ,,

Those previously found, for precipitated sulphur at the same temperature, were 512, 73, and 15. I have therefore concluded that the two curves are identical.

When the sulphur was removed from the circuit and a known resistance inserted, the calculated specific resistance was about one-fifth larger than that given by precipitated sulphur.

I have calculated the specific resistance from the experiments, more as an indication of the magnitude of the resistance at the boiling point, and of the changes that take place as the temperature varies, than as an accurate determination of specific resistance.

There are several circumstances which prevent the great accuracy usually expected in such cases. First the extreme difficulty of obtaining a steady temperature without exposing the electrodes to chemical action. Thus if the readings be taken at 350° C., by using a bath of boiling mercury it requires a considerable time to get the whole mass of sulphur to this temperature, the sulphur being a very bad conductor of heat and there being no agitation to assist. When the whole is steady and the electrodes are introduced, they cool the portion in contact with them, and it is necessary to wait until the temperature rises again. Hence arises an uncertainty, we may take it before the temperature is fully recovered, or we may delay too long and allow chemical action to commence. The same objection applies, in some measure, to boiling sulphur, but as the whole is in motion the recovery is quick.

Great care is necessary to prevent bubbles of gas rising up between the electrodes and so increasing the resistance.

Some error might also arise from the size of the electrodes, 3·35 cm. × 0·45 cm., distance 0·2 cm. They were as large as the quantities of pure sulphur obtained by nearly three months' work enabled me to use them.

With these reservations I give the specific resistance of melted sulphur, calculated from experiments with the three specimens mentioned.

Specific Resistances.

No. 1.	At 440° C.....	7·8	megohms.
2.	„	8·0	„
3.	„	7·3	„
2 & 3.	At 350° C.....	56·5	„
„	300° C.....	282·5	„

Boiling Point.

An objection has been raised to the curve found in the experiment on the boiling point of sulphur under varying pressures, on the ground that the vapour-pressure rises in a straight line, and that, therefore, the boiling point would give a straight line also.

It is usually stated in text-books that when the vapour-pressure of a liquid becomes equal to the pressure on the surface of that liquid it immediately begins to boil. If this is a scientific fact, the objec-

tion urged is good, and the vapour-pressure of any liquid and the boiling point of that liquid must always be on the same line. I think, however, that it is never absolutely correct, and sometimes it is very far from being true.

If we suppose a thin film of the liquid to be acted upon with a downward pressure produced by the air and an upward force produced by its vapour-pressure, these two forces, by hypothesis, equal and opposite in direction, can produce no motion in the film. Let the force necessary to produce this motion be called (a).

Besides the mere upward motion of the film in a bubble, there is an expanding action which draws out the substance of the bubble, and is resisted by it with force depending upon the nature of the liquid. Let this be called (b).

Finally, there is a certain amount of force required to burst the particles of the liquid apart when the bubble begins to form. Let this be (c).

We have, therefore, when bubbles are formed in any liquid, a force equal to the pressure on the surface of the liquid together with $a + b + c$.

If the viscosity of the liquid remains the same through the whole range of temperature, $a + b + c$ will remain the same, and the line for vapour-pressure and that for boiling point will be parallel, but if instead of this, the liquid changes from being a liquid as mobile as water to a thick viscous body, so stiff that the vessel containing it may be inverted without one drop of the substance being lost, $a + b + c$ will change also, and the two lines will not be parallel. The forces $a + b + c$ will be a function of the viscosity.

To test the truth of this reasoning, I carefully repeated the experiments, and found the results to agree with those previously obtained. At the same time, besides noting the pressures at which the bubbles began to form on the surface of the liquid at various temperatures, I observed the pressures at which these bubbles burst, and found that there was a considerable difference. Up to 280° C. it was 4 mm. of mercury, while at 296° C. it fell to 1 mm.,

or
$$\begin{aligned} A+B &= 4 \text{ mm. of mercury up to } 280^\circ \text{ C.} \\ A+B &= 1 \quad \text{,,} \quad \text{,,} \quad 296^\circ \text{ C.} \end{aligned}$$

I did not attempt to measure the force C, but I think it probable that it is much greater than A + B, and that the variation of these (A+B+C) in sulphur explains the form of the line found.

The sulphur molecule is known to undergo various changes, at one temperature containing six atoms, while at another only two enter into its formation. What are the molecular modifications that take place when it cools to a liquid, or when it assumes a semi-fluid state

and at last turns back again to liquid, we do not know. But when one of these changes is accompanied by a corresponding one in chemical activity, it appears to mark a point at which the complex molecules are being broken into others of less complex structure.

As this is the temperature at which the conductivity changes, I am inclined to suspect that the current is carried by the simpler molecules, as they break apart and recombine, acting, to a certain extent, the part of the different elements in an ordinary electrolyte. Supposing this to be the solution of the question, other elements that undergo similar molecular changes should give indications of a like nature, and I am at present engaged in work with the object of seeing if it is so.

May 23, 1889.

Professor G. G. STOKES, D.C.L., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

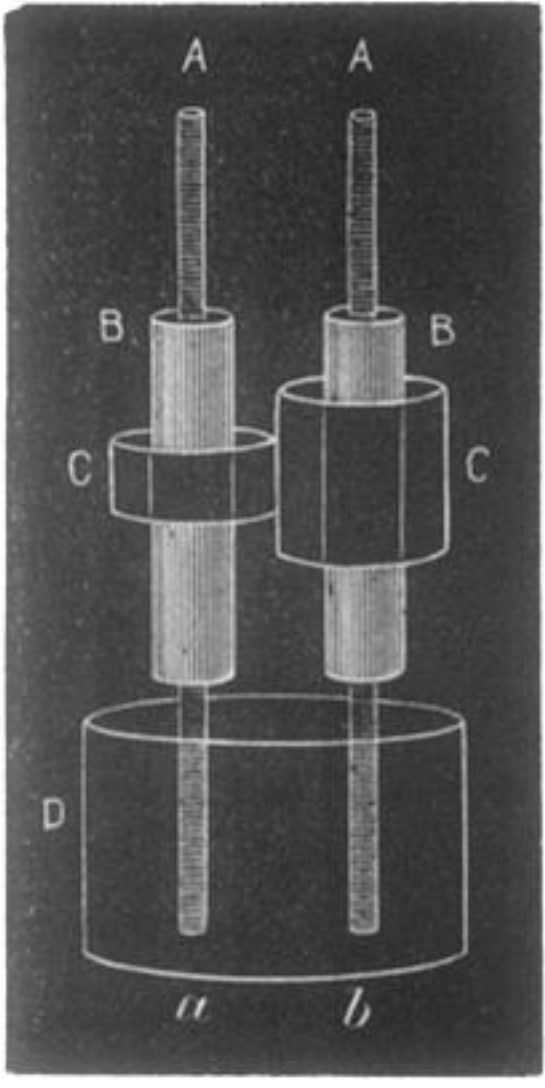
The Croonian Lecture was delivered as follows:—

CROONIAN LECTURE.—"Les Inoculations Préventives." By Dr. E. ROUX, Institut Pasteur, Paris. Delivered May 23,—MS. received May 23, 1889.

MESSIEURS,

Au mois d'Août, 1881, M. Pasteur faisait connaître aux membres du Congrès Médical International, réuni à Londres, les récents travaux de son laboratoire sur les inoculations préventives du choléra des poules et du charbon. Huit années sont presqu'écoulées depuis cette époque. Qu'est devenue l'œuvre commencée alors, a-t-elle justifié les espérances qu'elle faisait naître? Quelle place ont pris dans la science les principes nouveaux qui venaient d'y être introduits? C'est ce que M. Pasteur devait exposer devant vous aujourd'hui. Mais l'état de sa santé ne lui a pas permis de répondre à l'honneur que lui avaient fait le Président et le Conseil de la Société Royale, en le conviant à faire la lecture de cette année. Il a proposé au Président et au Conseil de votre Société d'accepter que je parle en son nom. Je ne saurais, Messieurs, vous parler, comme l'aurait fait M. Pasteur, de ces inoculations préventives qu'il a inventées, et je crains bien d'augmenter aujourd'hui, par mon discours, le regret que vous cause déjà son absence.

Je n'ai qu'un titre qui puisse expliquer que je sois à cette place,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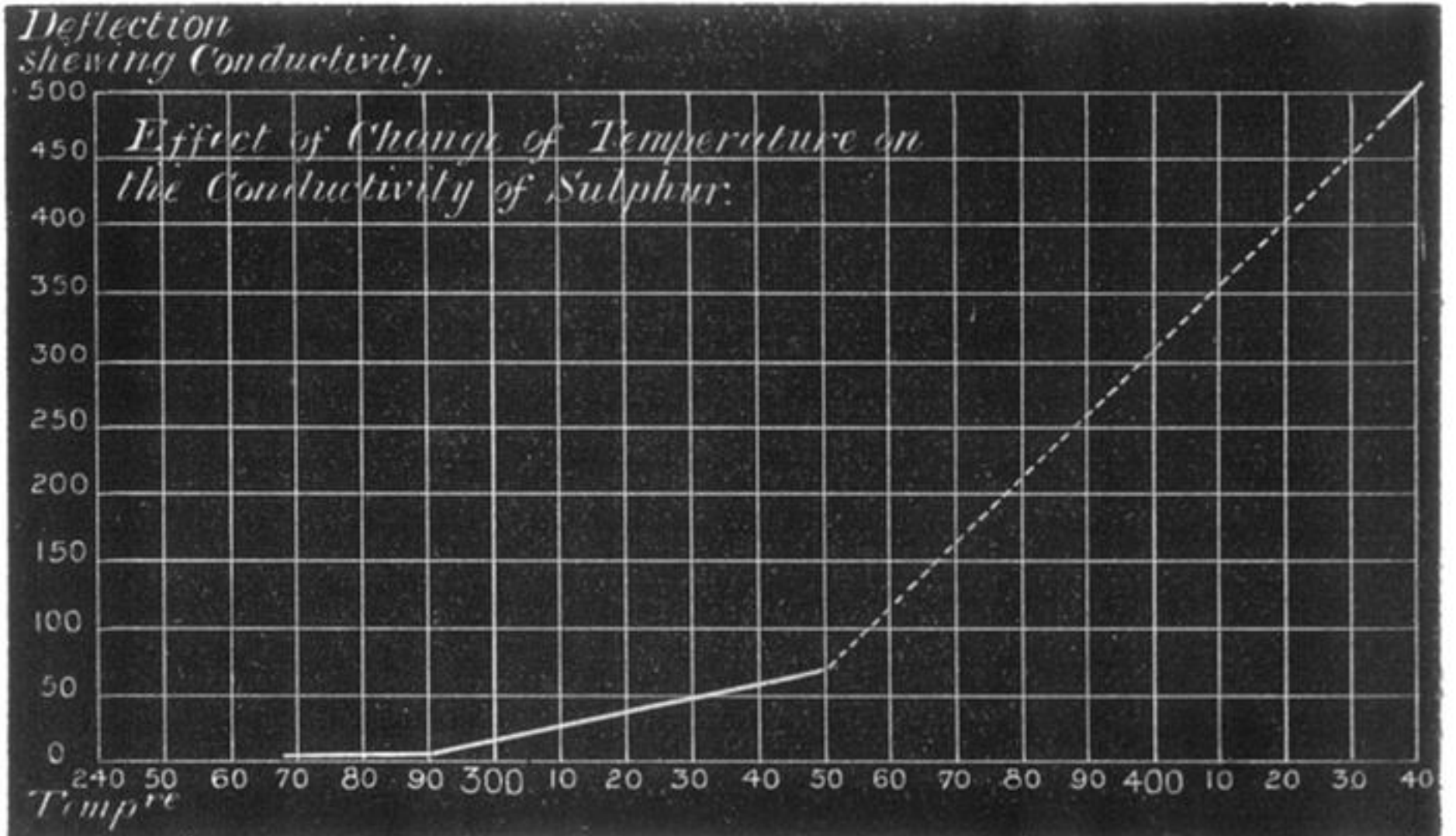
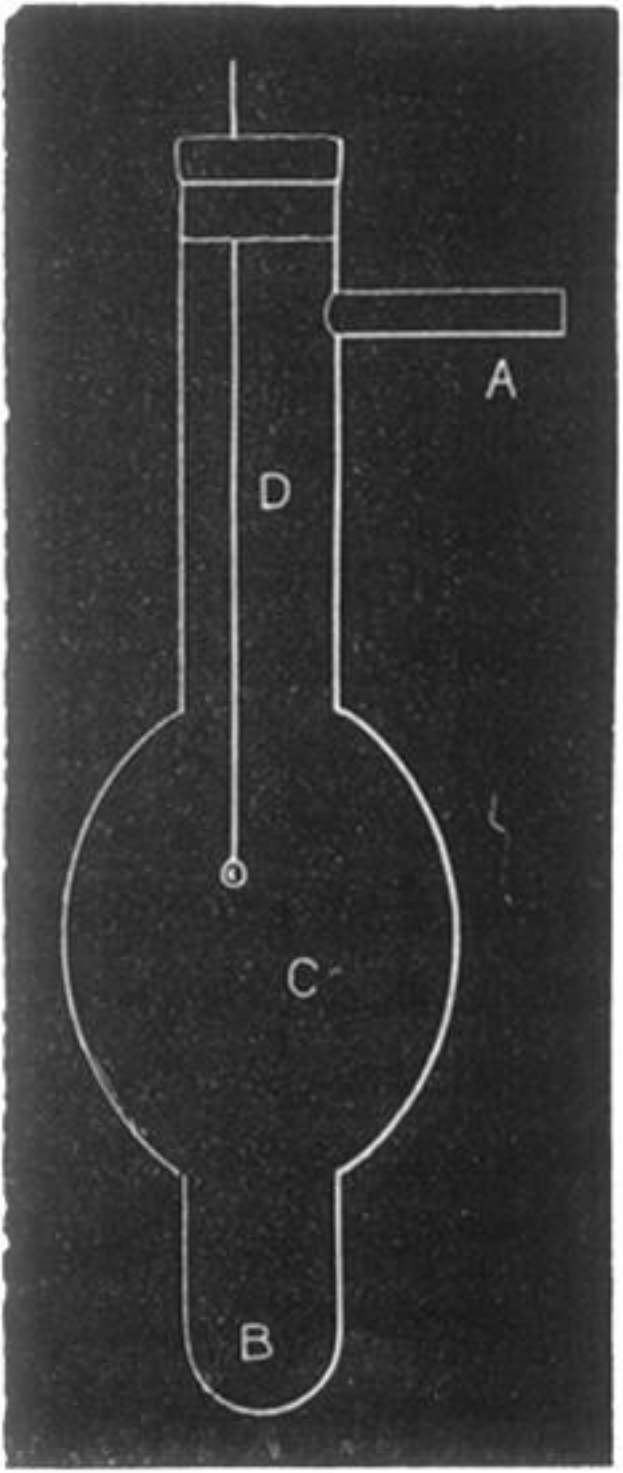


Boiling Point.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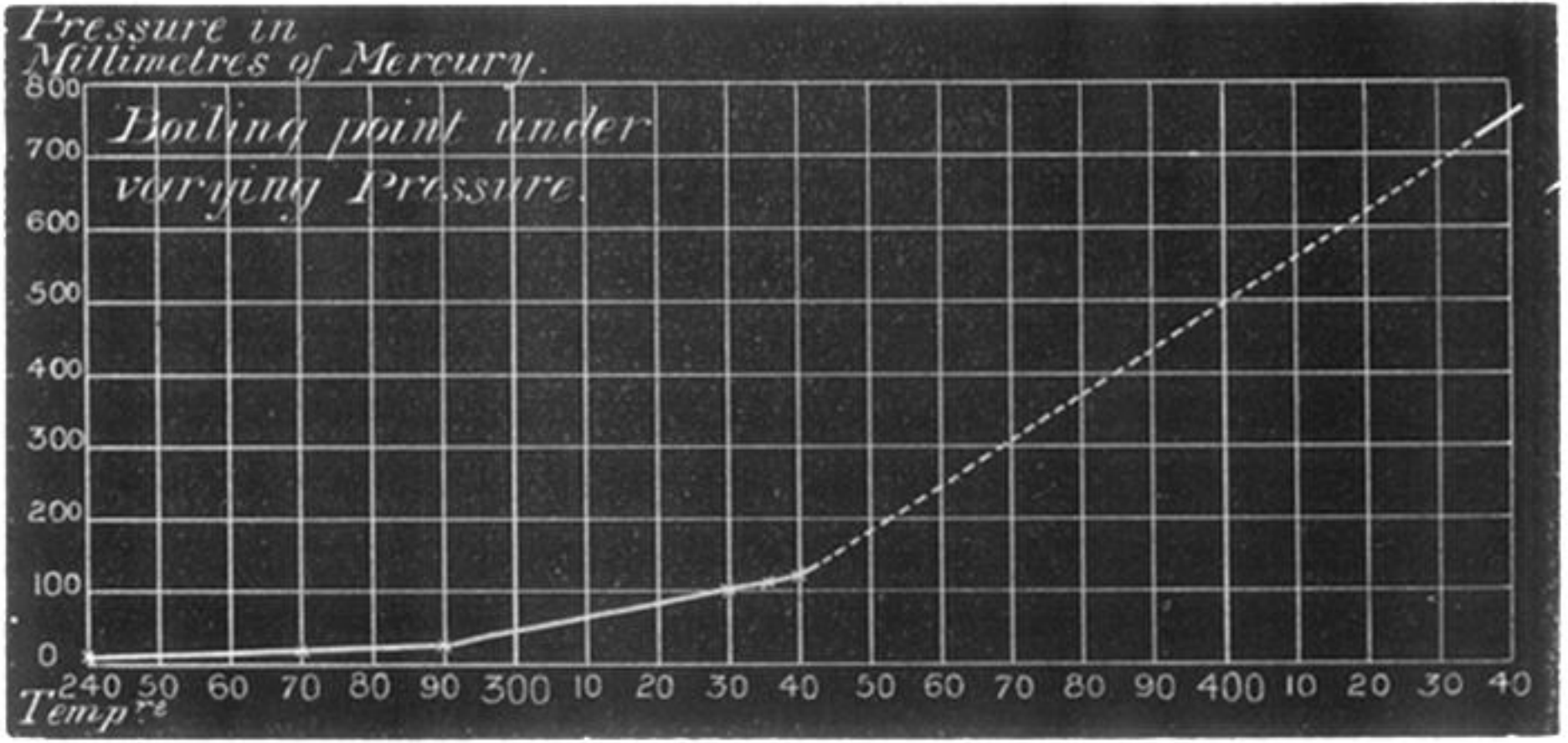
Pressure in
Millimetres of Mercury.
Boiling point under
varying Pressure.
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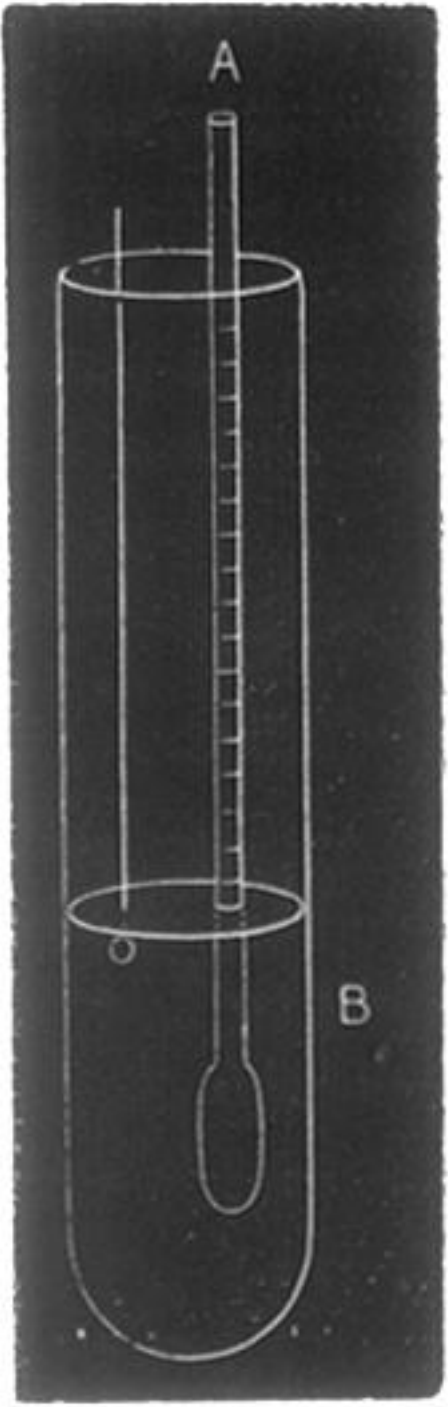
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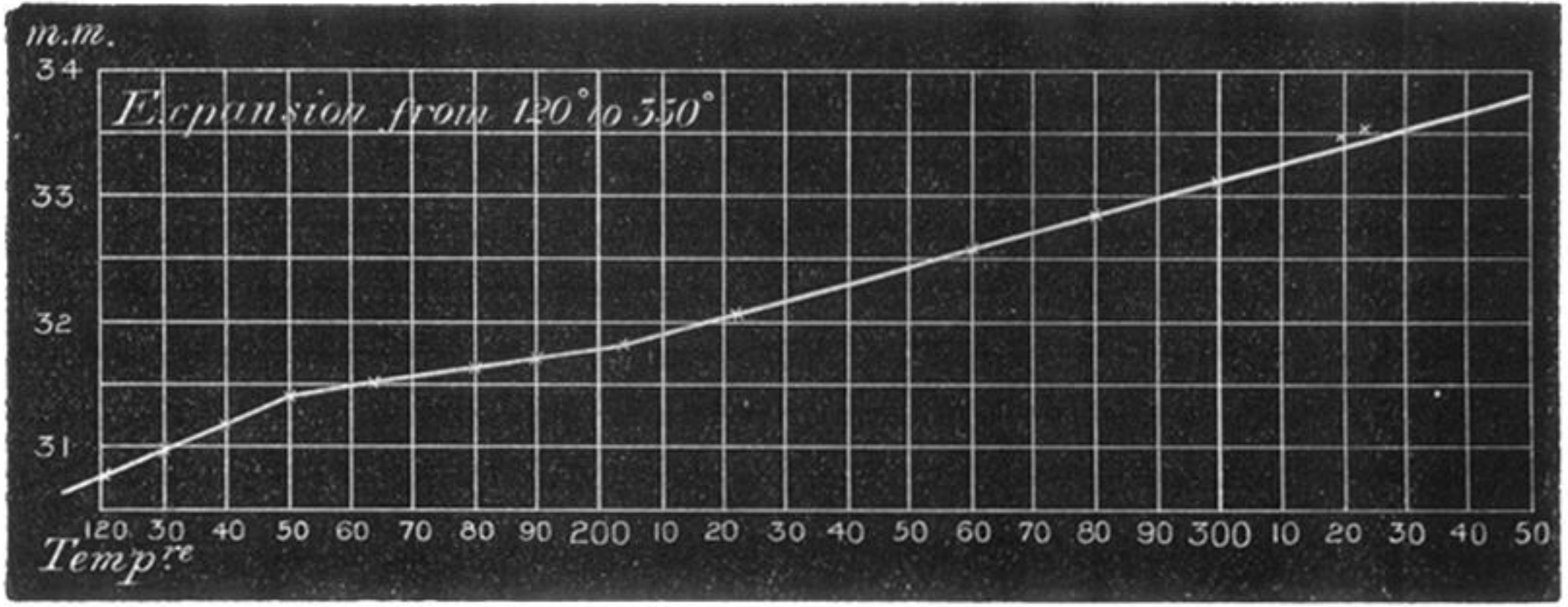
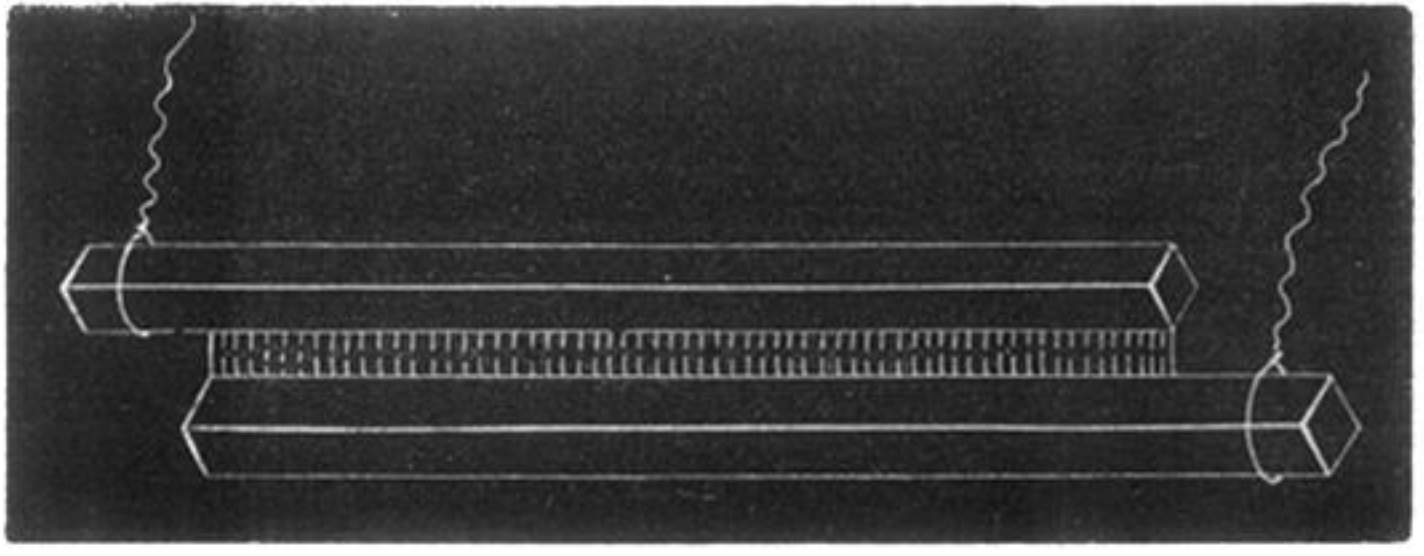
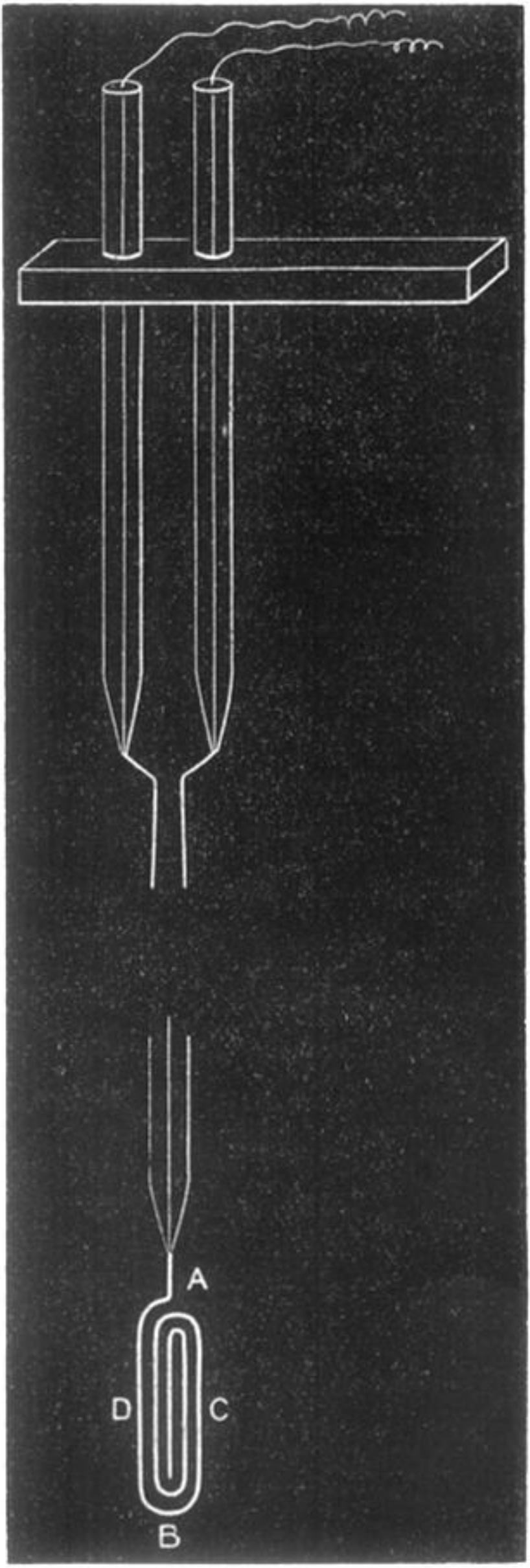


Chemical Affinity.

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